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This report contains a fit to the inversion spectrum of ammonia; data on HNO_3 in the infrared and microwave regions; data for the 1-0, 2-0 and 3-0 bands of NO.

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"Compilation of Spectroscopic Data for Trace Atmospheric Gases"

L. D. G. Young

Abstract

The object of this research was to compile spectroscopic data for the strongest bands of the molecules NO, NH_3 and HNO_3 and to put it in the format of the AFGL Atmospheric Absorption Line Parameters compilation. This has been done for the 1-0, 2-0, and 3-0 bands of NO (molecule 8). For the inversion spectrum of NH_3 (molecule 11); for the pure rotation spectrum, and the bands at 7.5μ and 11.3μ of nitric acid (molecule 12). These are all trace gases in the Earth's atmosphere. For NO and NH_3 papers have been submitted for publication (see appendices) while for HNO_3 a description of the data are of sufficient accuracy to permit a positive identification of the trace gas (pollutant) molecule.

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An Improved Fit to the Inversion Spectrum of $^{14}NH_3$

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Abstract

A Padé approximation with 19 terms is used to fit to measured line positions in the inversion spectrum of ammonia. It gives an order of magnitude better fit than an exponential (Costain) function with 21 terms, and two orders of magnitude better fit than a polynomial with 21 terms.

Introduction

In the course of preparing data for the AFGL trace atmospheric gas line parameter compilation, we discovered that Taylor's published[1] line positions for the ν_2 fundamental band of NH_3 at 10.5μ could be off as much as ~1.5 cm^{-1}, or 15,000 times the estimated error in measured line positions[2,3]. As a result, measured line positions were used in the data compilation[4,5], and we began to look into the reason for the discrepancy between the measurements and the calculations.

One of the first things we did was to look at the accurate microwave measurements of Poynter and Kakar[6]. They could not fit their own measurements of the inversion spectrum which "are good to ±0.005 MHz," with a standard deviation less than 0.034 MHz. They tried two approaches: First they assumed[7] that their data could be fit by power series in J(J + 1), the square of the total angular momentum, and K, the projection of the angular momentum on the symmetry axis

of the molecule. That is, the inversion energy could be represented by

$$E = BJ(J+1) + (C-B)K^2 + D_J J^2(J+1)^2 + D_{JK} J(J+1)K^2 + D_K K^4 + H_{JKK} J(J+1) K^4 + H_{JJK} J^2(J+1)^2 K^2 + H_{JJJ} J^3(J+1)^3 + H_{KKK} K^6 + \ldots \quad (1)$$

with the line positions being given by a similar power series in $J(J+1)$ and K^2. For a polynomial of this type, Poynter and Kakar found 10 terms gave a standard deviation of σ = 23.14 MHz, 15 terms gave σ = 2.308 MHz, and 21 terms gave σ = 0.228 MHz.

Next Poynter and Kakar tried the approach suggested by Costain[8] in a paper entitled "An empirical formula for the microwave spectrum of ammonia". Here the inversion frequency is represented by

$$\gamma = a \exp[bJ(J+1) + cK^2 + dJ^2(J+1)^2 + eJ(J+1)K^2 + fK^4 + \ldots] \quad (2)$$

Using a power law within the exponent gave Poynter and Kakar a somewhat better fit for 10 terms: σ = 0.495 MHz; however they could only get an order of magnitude improvement in going to 21 terms: σ = 0.039 MHz.

Clearly neither of these approximations could approach their experimental accuracy without a major increase in the number of constants being fit.

In referring to work on the NO molecule, Mizushima[9] noted that high order perturbations can lead to matrices in the form of a Padé approximant. Thus we decided this might be a useful approach for an empirical fit to the inversion spectrum of NH_3.

We first tried fitting the inversion energy with a fraction in which both numerator and denominator consisted of polynomials, such as given in

eqn. 1. While this approach gave a better fit, for the same number of constants, than either of the expressions for the inversion energy which Poynter and Kakar had used, we found we could get an even better fit if we used the following expression

$$E = [a + b_J F(J,K) + b_K K^2 + d_{JJ} F(J,K)^2 + d_{JK} F(J,K) K^2 + d_{KK} K^4 + h_{JJJ} F(J,K)^3 + h_{JJK} F(J,K)^2 K^2 + h_{JKK} F(J,K) K^4 + h_{KKK} K^6]$$
$$[1 + b_J^* F(J,K) + b_K^* K^2 + d_{JK}^* F(J,K) K^2 + d_{KK}^* K^4 + d_{JJ}^* F(J,K)^2 + h_{JJJ}^* F(J,K)^3 + h_{JJK}^* F(J,K)^2 K^2 + h_{JKK} F(J,K) K^4 + h_{KKK} K^6] \quad (3)$$

where $F(J,K) = [K^2 - J(J+1)]$.

Lines with K = 3, 6, 9, ... need to have an additional J-dependent term added, since they are affected by a K-type splitting[10,11]. Thus for K = 3 one must add

$$\Delta E_3 = (-1)^J f_3(J)[\alpha_1 + \alpha_2 J(J+1)]/[1 + \alpha_3 J(J+1)] \quad (4a)$$

where $f_3(J) = J(J+1)[J(J+1) - 2][J(J+1) - 6]$. For K = 6, the correction is[12]

$$\Delta E_6 = (-1)^{J+1} f_6(J)[\beta_1 + \beta_2 J(J+1)] \quad (4b)$$

where $f_6(J) = f_3(J)[J(J+1) - 12][J(J+1) - 20][J(J+1) - 30]$. For K = 9, the correction is

$$\Delta E_9 = (-1)^J f_9(J) \gamma_1 \quad (4c)$$

where $f_9(J) = f_6(J)[J(J+1) - 42][J(J+1) - 56][J(J+1) - 72]$. Using the

constants given in Tables 1 and 2, we found we could fit Poynter and Kakar's measurements with a standard deviation, for a line of unit weight, of 6.9 kHz, which is close to their nominal accuracy of 5 kHz. Figure 1 illustrates how the standard deviation drops as the number of parameters increases.

Poynter and Kakar's poor fit was due to three factors: First, they included several lines of lower accuracy from the NBS compilation[13]. Second, they gave all lines equal weight, even though they knew some lines were less accurate. When observations of unequal quality are combined, they should be given weights inversely proportional to the square of the error for each set of data. Third, they did not reject any bad, or discrepant, data.

Experience has shown that any iterative least-squares program must be able to reject aberrant data. As a practical matter, we have found that good results can be obtained if we reject data having a residual greater than 4σ (four standard deviations). We found the (12,1), (11,8) and (6,2) lines to have residuals of -339, -108 and -37 kHz, respectively; these are rejected by our 4-σ criterion.

Although the observed line positions are fit to a few kHz, the least-squares values of the parameters in Tables 1 and 2 have rather large errors. This is primarily due to the large correlation between numerator and denominator terms. Thus, it is necessary to give the coefficients several figures beyond the leading significant digits in their standard errors. One readily sees that, to retain 1 kHz accuracy up to quantum numbers on the order of 15, we must specify b's to about 10^{-5}, d's to about 10^{-7}, and h's to about 10^{-10}. We have been careful to give enough significant figures to allow others to reproduce our results.

The improved accuracy of our fit has allowed us to more accurately model the perturbations which affect the K = 3 and K = 6 lines, and to detect, for the first time, the perturbation of K = 9 at a signal/noise ratio of 3.4 standard deviations.

Table give the computed frequencies for the ammonia inversion lines in the microwave spectrum.

Acknowledgement

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Table 1. Coefficients in the Padé (rational) approximation to the inversion spectrum of ammonia.

Numerator Coefficients (MHz)		Denominator Coefficients (dimensionless)	
a	23785.8985 ± 0.0038		
b_J	79.750378±3.3871	$b_J^* \times 10^4$	-30.18 ± 1.42
b_K	21.145474±1.7309	$b_K^* \times 10^4$	-16.31 ± 0.73
$d_{JJ} \times 10^2$	10.355615±0.9322	$d_{JJ}^* \times 10^6$	2.328±0.516
$d_{JK} \times 10^2$	6.524901±0.4487	$d_{JK}^* \times 10^6$	4.598±0.210
$d_{KK} \times 10^2$	- 0.508608±0.2535	$d_{KK}^* \times 10^6$	1.113±0.077
$h_{JJJ} \times 10^6$	54.21590 ± 7.80	$h_{JJJ}^* \times 10^{10}$	5.56 ± 5.87
$h_{JJK} \times 10^6$	58.94479 ± 6.85	$h_{JJK}^* \times 10^{10}$	-45.93 ± 3.48
$h_{JKK} \times 10^6$	- 4.74446 ± 4.45	$h_{JKK}^* \times 10^{10}$	-21.45 ± 1.34
$h_{KKK} \times 10^6$	- 8.63503 ± 0.97	$h_{KKK}^* \times 10^{10}$	- 3.58 ± 0.33

Table 2. Coefficients in the additional terms for K = 3, 6, and 9.

$\alpha_1 \times 10^8$	36124.546 ± 3.64	MHz
$\alpha_2 \times 10^{10}$	206.4072 ± 18.3	MHz
$\alpha_3 \times 10^8$	77383.461 ± 645.	(dimensionless)
$\beta_1 \times 10^{15}$	16.562 ± 1.60	MHz
$\beta_2 \times 10^{18}$	17.896 ± 7.76	MHz
$\gamma_1 \times 10^{24}$	15.76 ± 4.61	MHz

Table 3. Computed inversion frequencies, in MHz.

(J,K)									
(0,0)	23785.898	(8,5)	18808.506	(12,4)	10293.664	(15,3)	1745.649	(17,11)	10098.589
(1,0)	23484.834	(8,6)	20719.218	(12,5)	11132.719	(15,4)	6123.323	(17,12)	12308.520
(1,1)	23694.498	(8,7)	23232.235	(12,6)	12251.327	(15,5)	6621.044	(17,13)	15258.377
(2,0)	22894.608	(8,8)	26518.978	(12,7)	13719.239	(15,6)	7285.768	(17,14)	19239.568
(2,1)	23098.822	(9,0)	13493.451	(12,8)	15632.812	(15,7)	8152.831	(17,15)	24679.860
(2,2)	23722.635	(9,1)	13612.161	(12,9)	18127.111	(15,8)	9283.656	(17,16)	32219.359
(3,0)	22038.186	(9,2)	13974.612	(12,10)	21391.623	(15,9)	10754.526	(17,17)	42840.263
(3,1)	22234.507	(9,3)	14376.814	(12,11)	25695.235	(15,10)	12674.208		
(3,2)	22834.187	(9,4)	15523.900	(12,12)	31424.948	(15,11)	15195.385		
(3,3)	23870.129	(9,5)	16798.133	(13,0)	7624.298	(15,12)	18534.909		
(4,0)	20948.005	(9,6)	18499.393	(13,1)	7690.939	(15,13)	23004.762		
(4,1)	21134.309	(9,7)	20735.454	(13,2)	7894.353	(15,14)	29061.188		
(4,2)	21703.358	(9,8)	23657.471	(13,3)	6438.586	(15,15)	37385.112		
(4,3)	22688.311	(9,9)	27477.934	(13,4)	8762.888	(16,0)	4371.533		
(4,4)	24139.414	(10,0)	11912.591	(13,5)	9476.068	(16,1)	4409.781		
(5,0)	19663.801	(10,1)	12017.175	(13,6)	10426.945	(16,2)	4526.511		
(5,1)	19838.348	(10,2)	12336.471	(13,7)	11673.167	(16,3)	10467.106		
(5,2)	20371.450	(10,3)	13296.338	(13,8)	13297.270	(16,4)	5024.619		
(5,3)	21285.275	(10,4)	13700.868	(13,9)	15412.488	(16,5)	5433.287		
(5,4)	22653.023	(10,5)	14822.521	(13,10)	18177.810	(16,6)	5973.898		
(5,5)	24532.983	(10,6)	16319.326	(13,11)	21817.983	(16,7)	6690.465		
(6,0)	18230.078	(10,7)	18285.440	(13,12)	26654.846	(16,8)	7618.098		
(6,1)	18391.553	(10,8)	20852.533	(13,13)	33156.855	(16,9)	8824.174		
(6,2)	18884.695	(10,9)	24205.295	(14,0)	6413.052	(16,10)	10397.183		
(6,3)	19757.575	(10,10)	28604.738	(14,1)	6469.077	(16,11)	12461.475		
(6,4)	20994.631	(11,0)	10390.745	(14,2)	6640.079	(16,12)	15192.770		
(6,5)	22732.424	(11,1)	10481.801	(14,3)	9670.850	(16,13)	18842.799		
(6,6)	25056.017	(11,2)	10759.774	(14,4)	7370.065	(16,14)	23777.341		
(7,0)	16693.445	(11,3)	10536.175	(14,5)	7969.300	(16,15)	30537.407		
(7,1)	16840.975	(11,4)	11947.247	(14,6)	8766.963	(16,16)	39941.436		
(7,2)	17291.493	(11,5)	12923.033	(14,7)	9814.364	(17,0)	3540.384		
(7,3)	18017.334	(11,6)	14224.648	(14,8)	11177.269	(17,1)	3571.452		
(7,4)	19218.462	(11,7)	15933.220	(14,9)	12951.053	(17,2)	3666.264		
(7,5)	20804.830	(11,8)	18162.361	(14,10)	15267.810	(17,3)	- 4178.909		
(7,6)	22924.936	(11,9)	21070.741	(14,11)	18313.662	(17,4)	4070.730		
(7,7)	25715.177	(11,10)	24881.927	(14,12)	22353.898	(17,5)	4402.457		
(8,0)	15100.072	(11,11)	29914.489	(14,13)	27772.295	(17,6)	4851.280		
(8,1)	15233.214	(12,0)	8954.654	(14,14)	35134.293	(17,7)	5422.466		
(8,2)	15639.763	(12,1)	9033.007	(15,0)	5328.180	(17,8)	6174.734		
(8,3)	16455.092	(12,2)	9272.186	(15,1)	5374.738	(17,9)	7152.230		
(8,4)	17378.104	(12,3)	10836.123	(15,2)	5516.837	(17,10)	8426.974		

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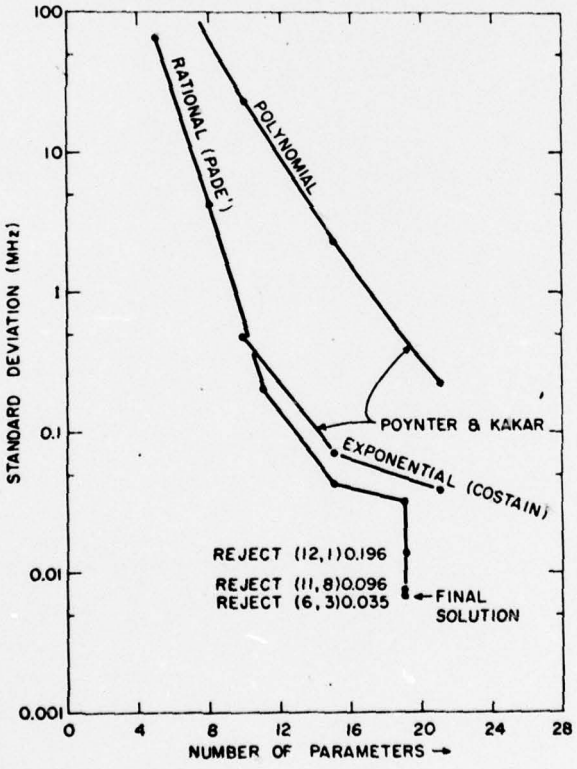
List of Figures

Figure 1. Standard deviation for the fit to the inversion spectrum of ammonia as a function of the number of parameters used in the fit.



Nitric Acid Vapor (Molecule 12)

The nitric acid molecule is approximately an oblate symmetric top, since the ground state rotational constants are A_0=0.4340 cm^{-1}, B_0=0.4036 cm^{-1} and C_0=0.2088 cm^{-1}. The C axis is perpendicular to the plane of the molecule, while the dipole moment lies in the plane. Note that $A \approx B \approx 2C$. This gives rise to a rotational spectrum which is interesting, since a large number of coincidences of line positions occur. It results in a very simple spectral pattern under moderate resolution. One can write the energy, E, as

$$E = 0.41865\ J(J+1) - 0.20985K_1^2 + \text{Smaller terms}$$

(Flemming, 1974). This spectrum has the general appearance of that for a diatomic molecule with a line spacing of ~ 0.4 cm^{-1}.

The line positions are given by Flemming and Wayne (1975). They published a spectrum taken between 10 and 40 cm^{-1} with a resolution of 0.05 cm^{-1}. The pressure was 4.5 torr and the pathlength was 1 meter. Using the values of the halfwidth for self broadening (α_s = 0.8 cm^{-1}) and nitrogen broadening (α_f=0.13 cm^{-1}) as reported by Brockman et al. (1978), and assuming a square root absorption law, we have derived values for the line intensity. The portion of the 7.5μ band measured in the laboratory by Fontanella et al. (1975) for a total pressure of 66 mb and amounts of HNO_3 vapor ranging from 0.27×10^{17} to 0.44×10^{18} molecules/cm^3, has also been used to derive line intensities for that band. It also appears to have a "line" spacing of $\sim$0.4 cm^{-1}. The lower resolution data of Goldman et al. (1971) and Moskalenko (1972) have not been used, as the individual spectral lines are not resolved. However, the integrated intensity of the 7.5μ band, obtained by Goldman et al., was used to check the line intensities derived from the spectra published by Fontanella et al. Approximate values of the rotational quantum numbers are given in the AFGL trace-gas compilation. The line strengths for both the pure rotational spectrum and the 7.5μ band are estimated to be accurate to ± 20%.

Brockman et al. (1978) have made very high resolution measurements of a portion of the 11.3μ band. No quantum numbers have been assigned to the 1080 lines measured. They estimated the uncertainties of the line strengths as ± 20%, and of the line positions as ± 0.005 cm^{-1}. The pure rotational line positions have an estimated precision of ± 0.003 cm^{-1}, while the positions of the lines in the 7.5μ band, are considerably less certain, having been read off of the published spectra; they are only accurate to ± 0.1 cm^{-1}.

In putting the band identification on the IBM cards, we ran into the problem of not enough room in the card format for all the quantum numbers to be listed in the usual way. I have given the band location in microns and the lower (ground) state simply represented as 0.

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Calculation of Spectroscopic Data for the V=0 and V=1 States of Nitric Oxide

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Abstract

The calculation of line positions, energy levels and line intensities for the NO fundamental, done for the AFGL atmospheric trace gas data tape, is presented. A simultaneous, least-squares fit to measured frequencies for the fundamental and satellite bands of $^{14}N^{16}O$, to its microwave spectrum, and to two-photon spectra in the microwave region has yielded new spectroscopic constants. The eigenvectors obtained were used to compute line intensities for these bands. Line halfwidths, based on a linear fit to the measurements of Abels and Shaw, were used in the data compilation.

[†]Participant USAF-ASEE Summer Faculty Research Program, at the Air Force Geophysics Laboratory, 1976.

Introduction

There has been a group of papers recently on the NO fundamental. This interest derives from the facts that nitric oxide is a trace (pollutant) gas in the earth's atmosphere;[1-3] and is also one of a few molecules with a $^2\Pi$ electronic ground state and hence is inherently interesting to spectroscopists.[4-16] Our calculations differ from other recently published results since we have included microwave data in addition to data on the fundamental. We have also included higher-order terms (e.g. H_v) in the expression for the rotational energy levels.

Recent high resolution measurements by Valentine et al.[10] on the infrared spectrum of NO have yielded substantially more accurate line positions for the two fundamental bands ($^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$ and $^2\Pi_{3/2} \leftarrow {}^2\Pi_{3/2}$) and their satellite bands ($^2\Pi_{1/2} \leftarrow {}^2\Pi_{3/2}$ and $^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$). In addition to these measurements, Pine and Nill have recently measured (but not yet published) lambda-doubling in the fundamentals, using two-photon spectroscopy which has the accuracy inherent to microwave spectroscopy. By combining these new data with the older microwave measurements[17-25] on the ground states [the $^2\Pi_{1/2}$ J= 1/2→3/2 and 3/2→5/2 lines measured by Gallagher and Johnson[25] and the $^2\Pi_{3/2}$ J = 3/2 → 5/2 line measured by Favero et al.[26]], we believed that accurate eigenvectors and energy eigenvalues could be obtained for both the v = 0 and the v = 1 states. Our data base consisted of 298 measured frequencies, which were weighted according to the accuracy of the experimental measurements. The weights used in the computer program are based on the reciprocal of the squares of the stated errors; lines having residuals

greater than four standard deviations were flagged and rejected for the next iteration. In our original calculations, we included the lines in the pure rotational spectrum[26,27] and older measurements of the fundamental band in the infrared.[20-29]

Line-Frequency Calculations

The appropriate theory of $^2\Pi$ electronic ground states dates back to Van Vleck.[30] For NO, the two ground states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are perturbed by an upper $^2\Sigma$ electronic state. Keck[29] and James[28] have indicated the matrix elements for the appropriate two 3 x 3 matrices of the Hamiltonian,* xiz.

$$H_r + A\,(L\cdot S) = \begin{bmatrix} H_{11}^{s,a} & H_{12}^{s,a} & H_{13} \\ H_{21}^{s,a} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{bmatrix} \qquad (1)$$

Here the superscripts s and a refer to the symmetric and antisymmetric basis functions; also,

$$H_{11}^{s,a} = E_{\Sigma-\pi} + B_\Sigma\,(J + 1/2)^2 \pm B_\Sigma\,(J + 1/2), \qquad (2a)$$

$$H_{12}^{s,a} = a_e + 2b_e \pm 2b_e\,(J + 1/2), \qquad (2b)$$

$$H_{13} = 2b_e\,[\,(J + 3/2)(J + 1/2)\,]^{1/2}, \qquad (2c)$$

$$H_{22} = G_v - A_v/2 + (J + 1/2)^2(B_v - A_J) - (J+1/2)^4 D_v + (J+1/2)^6 H_v, \qquad (2d)$$

$$H_{23} = [\,B_v + 2D_v - 2Dv(J + 1/2)^2\,]\,[\,(J + 3/2)(J - 1/2)\,]^{1/2}, \qquad (2e)$$

$$H_{33} = G_v + A_v/2 - 2(B_v + 2D_v) + (J + 1/2)^2\,(B_v + 4D_v + A_J) - (J + 1/2)^4 D_v + (J + 1/2)^6 H_v, \qquad (2f)$$

*See also Dousmanis, Sanders and Townes.[23]

where the upper sign in egn (2a) and (2b) refers to the s matrix element and the lower sign refers to the a matrix element. Here the constants G_v, B_v, D_v, and H_v have their usual meaning, A_J allows for the J dependence of the spin-orbit interaction constant A, and A_v allows for its dependence on vibrational state. The Λ-doubling parameters are $a_e = \langle \pi | A\, L_y | \Sigma \rangle$ and $b_e = -\langle \pi | B\, L_y | \Sigma \rangle$.

Holding the constants $E_{\Sigma-\Pi}$ and B_Σ fixed, and using the spectroscopic constants for the fundamental reported by Olman et al.[31] as starting values, we proceeded to do an interative least-squares correction of the parameters given in Table 1. The measured line frequencies and doublet splittings were compared with frequencies computed from the difference of energy eigenvalues between the upper and lower states. The constants a_e and b_e were poorly determined if the microwave measurements of lambda doubling in the fundamentals were not included. Giving these measurements a weight of 500 (compared to a weight of 1 for the infrared data) resulted in well-determined values for a_e and b_e. The values of B_Σ and $E_{\Sigma-\Pi}$ could be varied by five percent with a negligible effect on the values of the $^2\Pi$ state spectroscopic constants obtained on fitting the data. The standard deviation found for the frequency/lambda-doubling fit was 0.0011 cm^{-1} for a measurement of unit weight.†

Originally, the measurements of Keck[29] and James[28] were included. Both of these sets of data had substantially higher residuals than the data of Valentine et al.[10] It was decided that James' and Keck's data were contributing mostly "noise" to the solutions, so these data sets were dropped.

†The microwave lines have a typical weight of 7000; Pine's measurements of lambda doubling have weight ~ 1000; Valentine et al. measurements have weight 2 except for "bad lines" which have weight 0.5.

Recent measurements of 19 NO lines made using a CO laser [96,11,12] were given weights comparable to those of the 273 lines measured [10] in the infrared. The pure rotation lines measured by Palik and Rao [26] and by Hall and Dowling[27] had large systematic deviations and were dropped from the final solution. The relatively large errors and hence low weights for these lines leads us to believe that Rabach'e calculations [15] are inaccurate, since he used the pure rotational lines in his fit to the molecular constants for NO. In addition, his calculations assume the zero energy level lies midway between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states and, therefore, his computed energy levels are inaccurate by at least $\sim A_v/2$.

Table 1 gives the values obtained for the spectroscopic constants. The constants of Valentine et al.,[10] using the theory of Albriton and Zare, are given for comparison. With the exception of H_v, we have a smaller standard deviation for our constants than the latter have. Finally, it should be noted that the use of effective constants[30] in fitting Keck's measurements[29] of the fundamental yield values with considerably larger errors, but taking that into account, give results in agreement with the present calculations.*

By including the very accurate microwave data, we have obtained much greater accuracy for the low-order rotational constants and the Λ-doubling constants.

Line Intensity Calculations

When we diagonalize the Hamiltonian matrices, we obtain the eigenvectors $U^{s,a}(^2\pi_{1/2}, v, J)$, $U^{s,a}(^2\pi_{3/2}, v, J)$ and $U^{s,a}(^2\Sigma, v, J)$, in addition to the energy eigenvalues. Using the $^2\Pi$ eigenvectors, it is straightforward to compute the line strengths using the electric dipole moment transition probabilities for symmetric tops.[33] For the two fundamental

* The results are indicated in Table 2.

bands, $^2\Pi_{1/2} - {}^2\Pi_{1/2}$ and $^2\Pi_{3/2} - {}^2\Pi_{3/2}$, we obtain essentially the same line strengths as James.[34] We compared our calculated line strengths with James' for the two satellite bands. For the satellite bands, James only published line strengths for the $^2\Pi_{3/2} - {}^2\Pi_{1/2}$, transition. Our present calculations yield somewhat different values for the line strengths. We can reproduce James' results by setting the lambda-doubling constants a_e and b_e equal to zero and using the spectroscopic constants we obtained for the ground state as the constants for both the upper and lower vibrational states. Goldman and Schmidt[8] noticed a similar result in their calculations as compared with James.

Line Halfwidths Used in the AFGL Data Compilation

A comparison of line widths measured by Hochard-Demolliere et al.[35] by Ables and Shaw[36] with the linewidths calculated by Tejwani et al.[37] show considerable discrepancies. In our judgement, a linear fit to the measurements of Ables and Shaw should give reasonably good values for atmospheric transmission calculations.

Discussion

By diagonalizing the Hamiltonian given in eqn. (1) and fitting the computed energy eigenvalues to experimentally observed line positions, we have obtained quite precise energy values of the v" = 0 and the v' = 1 states of $^{14}N^{16}O$. In addition, by using the eigenvectors obtained in the above process, we have computed accurate line strengths. Valentine et al.[10] and Johns et al.[14] have made calculations very similar to ours. We give a comparison of the results in Table 1. This shows that our values for the constants, as a whole, have values intermediate to those found by these other authors. The values of a_e and b_e were computed from their published values

of p and q and $E_{\Sigma\Pi}$ as given by Herzberg.[33] The discrepancy between our calculations and those of Valentin et al.[13] for values of H_v and A_J is puzzling, since these constants are determined from the high J lines and we have employed the same data. The differences in the other constants can be attributed to our inclusion of measurements in the microwave region.

The calculations of Meerts[39] and Kristiansen[16] employed a different perturbation scheme and a different set of spectroscopic parameters. The simplest way to compare these results with ours is in terms of effective constants. This is done in Table 2. Kristiansen[16] used the data of Keck[29] and of James and Thibault[28] for infrared data; he used those of Hall and Dowling[27] for the rotational spectrum, and the same data as we used for the microwave lines. In Kristiansen's determination of line parameters for NO, the spectroscopic constants D_v and H_v were not included in his fit of 16 parameters to 159 lines.

Our calculations included these parameters, and we fit to 298 lines and lambda splittings. Meerts[38-40] fit the hyperfine splittings of NO lines in the microwave region, using 91 observed transitions in the frequency range from 0.6 MHz to 258 GHz. He required 22 molecular constants to describe the observations.

While our constants a_e and b_e show a slight dependence on the vibrational state, one would not have expected this. However, when these constants are set equal to the mean value for the two vibrational states, the rms error in a line position of unit weight increases from σ = 0.000647 to 0.005241. In addition, the program rejects all of Pine's measured Λ splittings in the R-branch of the 1/2-1/2 subband. Thus, the <u>difference</u> between the a_e (and b_e) values for the v = 0 and v = 1 states is both statistically significant and well determined.

The input data for the AFGL atmospheric trace gas tape should be accurate to better than 0.0004 cm^{-1}, which is about the accuracy routinely available in CO laser-line data.

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Table I. Spectroscopic constants for N_o

present results $\sigma = .000647$	Valentine[10]	Johns et al.[13] [14]
B_{vo} 1.69613891 ±.00000116	1.6961360 ± .0000032	1.6961087 ± .0000040
D_{vo} 5.49149×10^{-6} ±.00374	5.47498×10^{-6} ±.00055[x]	5.495×10^{-6} ±.013
H_{vo} 2.072×10^{-11} ±.258	1.346×10^{-11} ±.300	
A_{vo} 122.94865 .00145	123.02774 ±.00011	122.8778 ±.0490
A_{jo} 1.75852×10^{-4} .00332	3.47621×10^{-4} .00050	-9.89×10^{-5}
a_{eo} 90.130 ±.352	89.11[b] ±.05	116.3[b] + 0.3
b_{eo} .71564 ±.00279	0.7130[b] ±.0004	0.608[b] ±.056
$E_{\Sigma\Pi o}$ 44,000	44,000[a]	44,000[a]
$B_{\Sigma o}$ 1.9870		
G_{v1} 1875.97116 ±.00041	1875.97240 ±.00007	1875.9725 ±.0010
B_{v1} 1.67856953 .00000121	1.6785673 ±.0000030	1.6785438 ±.0000107
D_{v1} 5.50779×10^{-6} .00333	5.49278×10^{-6} .00050	5.513 ±.013 $\times 10^{-6}$
H_{v1} 1.837×10^{-11} ±.216	1.209×10^{-11} ±.255	
A_{v1} 122.70577 ±.00304	122.78249 ±.00011	122.6427 ±.0440
A_{j1} 1.70448×10^{-4} .00304	3.36993×10^{-4} .00050	9.91×10^{-5}
a_{e1} 90.236 ±.276	90.79[b] ±.11	115.7[b] ±0.3

Table I. Spectroscopic constants for N_o

present results	Valentine[10]	Johns et al [13] [14]
b_{el} .72093 ±.00221	0.7366[b] ±.0004	0.585[b] ±.056
$E_{\Sigma\Pi}$ 46,300	46,300[a]	46,300[a]
B_{Σ} 1,9706		

[a]Assumed value for the energy difference between the lower (Π) state and the upper (Σ) perturbing state

[b]Computed from values of the constants p and q, using the assumed value of $E_{\Sigma\Pi}$

Table 2 Effective Constants for N_o

	James and Thibault[28]	Keck[29]	Valentin[10]	Young and Young[32]	Kristiansen[16]	Meerts[38-40]
B_o	1.696285	1.696101	1.6960905	1.696121		
B_1	1.678735	1.678527	1.6785207	1.678543	1.696083[e]	1.696104[e]
$D_o \times 10^6$	5.9185	5.470	5.47784	3.519		6.17
$D_1 \times 10^6$	5.9320	5.485	5.49277	5.526		
$H_o \times 10^{10}$	3.56	0	1.258	0.24		
$H_1 \times 10^{10}$	3.195	0	0.870	0.18		
A_o	123.160	123.1881	123.1396		123.1394[e]	123.160
A_1	122.911	122.9466	122.8945			
a_e		89.11[e]	89.946[e]		90.353[e]	89.4962[e]
b_e		0.712[e]	0.7248[e]		0.7254[e]	0.7228[e]
$E\Sigma\pi$		44,000	44,000		44,000	44,000

[e]These values were converted to the notation used in the present paper.

Calculation of Spectroscopic Data for the v=2 and v=3 States of Nitric Oxide

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Abstract

The calculation of line positions, energy levels and line intensities for the NO overtone bands 2-0 and 3-0, done for the AFGL atmospheric trace gas data tape is presented. A simultaneous least squares fit has been made to the measured frequencies of the overtone bands, using previously determined constants for the ground (v=0) state. This has resulted in new spectroscopic constants for the v=2 and v=3 states. The eigenvectors were used to compute line intensities, and the same line halfwidths as were used for the fundamentals are used for the overtone bands.

Introduction

In an earlier paper[1] we reported the results obtained from a least-squares fit to the fundamental band, and the details of the line frequency fit are presented there. The same computer program was used for the overtone bands. Once again, we fit to the recent laboratory measurements of NO line positions given by Henry et. al.[2]. These latter authors used the method of Zare et. al.[3] to obtain spectroscopic constants for the three bands (1-0), (2-0) and (3-0). However, for these bands, they only included lambda doubling of the lines as a correction to the unsplit line positions. Our computer program includes Λ-doubling explicitly.

The Overtone Bands for the (2-0) band, 143 lines have been published by Henry et. al. Blends have been given a weight of zero in our calculations. All other lines have a weight = 1.0. Our fit to their measured frequencies gives a standard deviation of 3.7×10^{-4} cm^{-1}, while Henry et. al. report a standard deviation of 5×10^{-4} cm^{-1}.

There is a reason for our improved fit to their data: Henry et. al. were forced to assume that the lambda-doubling parameters p and q (analgous to our a_e and b_e) had the same values for the vibrational states v=1, v=2, and v=3. We don't have to make this assumption for the (2-0) band.

For purposes of comparison with the data of Henry et. al., we did assume the v=1 constants could be used for the (2-0) band. This produced a larger standard deviation, 4×10^{-4} cm^{-1}, than our fit where both a_e and b_e were allowed to vary. For this band, both a_e and b_e were fairly well determined.

For the (3-0) band, Henry et. al., only published frequencies for 112 lines and lambda splittings. Here, they only measured two lines in the Q branch of the $^2\pi_{\frac{1}{2}}$-$^2\pi_{\frac{1}{2}}$ band with lambda doubling. This simply is too few data for

our program to find both a_e and b_e. Since a_e is simply a constant in our Hamiltonian, we can hope to determine it. The constant b_e appears as a coefficient of terms involving the rotational quantum number J and the J values of the split lines, for the $^2\pi_{\frac{1}{2}}$-$^2\pi_{\frac{1}{2}}$ band, are only J = 3/2, and J = 5/2. As a result we can't get a good value for b_e. We have assumed values for b_e fixed at 0.74, 0.75 and 0.76 cm^{-1}. The three fits to the frequencies measured all had a standard deviation of $\sigma = 5.81 \times 10^{-4}$ cm^{-1}, so we present our results in Table 1, only for $b_{e_3} = 0.75$. The constants of Henry et. al.[2], also shown in Table 1, had a standard deviation of $\sigma = 7 \times 10^{-4}$cm. We believe our smaller standard deviation resulted from including H_v terms in the rotational energy expression and our use of smaller values for the lambda doubling parameters.

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Table 1. Spectroscopic constants determined from a least squares fit to the 2-0 and 3-0 bands of NO (in cm^{-1}).

			Henry et al			Henry et al
		$\sigma = 3.7\times10^{-4}$	$\sigma = 5.0\times10^{-4}$	$\sigma = 5.8\times10^{-4}$		$\sigma = 7\times10^{-4}$
		G_{v_2} 3723.84437	3723.85322	G_{v_3} 5543.6849		5543.69295
		0.00207	0.00013	0.0023		
B_{v_0}	1.696 138 93	B_{v_2} 1.660 969 56	1.660 9632	B_{v_3} 1.643 335 96		1.643 322 87
		0.000 001 47		0.000 001 81		
$D_{v_0}\times10^6$	5.4916	$D_{v_2}\times10^6$ 5.52892	5.49950	$D_{v_3}\times10^6$ 5.55575		5.51907
		0.00246		0.00607		
$H_{v_0}\times10^{11}$	2.077	$H_{v_2}\times10^{11}$ 2.350		$H_{v_3}\times10^{11}$ 3.16		
		0.181		0.53		
A_{v_0}	122.948 671	A_{v_2} 122.46545	122.52708	A_{v_3} 122.19773		122.26106
		0.00415		0.00423		
$A_{J_0}\times10^4$	1.7587	$A_{J_2}\times10^4$ 1.6479	3.26362	$A_{J_3}\times10^4$ 1.5986		3.15261
		0.0029		0.0144		
a_{e_0}	90.1299	a_{e_2} 87.085	92.376[b]	a_{e_3} 88.20		94.542[b]
		1.068		1.51		
b_{e_0}	0.71564	b_{e_2} 0.74786	0.7550[b]	b_{e_3} 0.75		0.7727[b]
		0.00874				
$E_{\Sigma\pi}$	44,000	$E_{\Sigma\pi}$ 48,600	48,600[a]	$E_{\Sigma\pi}$ 50,900		50,900[a]
B_Σ	1.987	B_Σ 1.954		B_Σ 1.938		

[a] assumed [b] computed using $E_{\Sigma\pi}$